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# THE THERMAL DECOMPOSITION REACTIONS OF BIS-(PYRIDINE-2-ALDOXIME)-COPPER(II) COMPLEXES

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The thermal properties of some complexes of copper(II) with pyridine-2-aldoxime (HPAO), where the ligand appears either as the ion ($PAO^-$) or as a neutral molecule, were determined in vacuo and in dynamic nitrogen and oxygen gas atmospheres. The study was carried out by thermoanalytical (TG, DTG. DTA), spectroscopic and spectrometric (UV-visible, IR, diffuse reflectance, mass) techniques.

The initial decomposition temperature is influenced by the number of acid hydrogens in the complex; the thermal stability sequence in vacuo is:

$$[Cu(PAO)_2H]Cl > [Cu(PAO)_2H_2]Cl_2 > [Cu(PAO)_2]$$

The thermal decomposition reactions occur in several separate steps, the first of which gives rise to partial ligand decomposition, the reduction of copper(II) to copper(I), and the conversion of the residual pyridine-2-aldoxime into acid amide.

Several papers have been published on the complexes of metal ions with pyridine-2--aldoxime ($C_6H_6N_2O$; HPAO). Some copper(II) complexes with this ligand have been studied in aqueous solution, or precipitated and characterized using IR, diffuse reflectance, polarographic and potentiometric techniques [1–7], but no data have been reported on the thermal stabilities and decomposition reactions.

Following thermoanalytical studies of the complexes of 3 d metal ions with organic ligands [8–11], in this paper we report results on the thermal behaviour of the complexes $[Cu(C_6H_5N_2O)_2H_n]Cl_n$ (where $n = 0$, 1 or 2). The study has been carried out by thermogravimetry, differential thermal analysis and mass spectrometry; the proposed decomposition mechanisms are supported by analysis of the stable intermediates obtained by interruption of the heating of the samples at the appropriate temperatures.

## Experimental

### *Apparatus*

The thermal measurements were carried out by means of a Perkin–Elmer TGS-2 thermal analyser and DTA 1700. TG runs were made in vacuo and in dynamic nitrogen or oxygen gas atmospheres with a flow rate of about 50 ml $\mathrm{min}^{-1}$; DTA runs were made in dynamic nitrogen or oxygen gas atmospheres. The heating rate was 5 or 10° deg. $\mathrm{min}^{-1}$, with samples of 4–6 mg.

Mass spectra were obtained on a Hewlett–Packard 5982 mass spectrometer, coupled with a Hewlett–Packard 5934 A data system, operated in the electron impact mode; source $p \cong 5 \cdot 10^{-7}$ torr; electron energy 70 eV; the samples were introduced via the direct insertion probe.

The reflectance, IR and UV spectra were recorded using a Beckman DBG spectroreflectometer, a Perkin–Elmer 125 grating infrared spectrophotometer and a Perkin–Elmer 320 UV-visible spectrophotometer, respectively.

The acidity of the solutions was checked with an Amel 333 potentiometer, equipped with an Ingold type 201 glass electrode and an Ingold type 202 calomel reference electrode.

### *Compounds*

Monohydrogen bis-(pyridine-2-aldoxime)-copper(II) chloride

$$([\mathrm{Cu}(\mathrm{C_6H_5N_2O})_2\mathrm{H}]\mathrm{Cl} = [\mathrm{Cu(PAO)_2H}]\mathrm{Cl})$$

was prepared according to the method of Liu [2]; the same compound was obtained, in excellent yield, by the slow addition of a solution of copper(II) chloride dihydrate (0.0025) mol in about 10 ml 95% ethanol) to a solution of pyridine-2-aldoxime (0.01 mol in about 50 ml 95% ethanol). This complex is a green crystalline powder soluble in water, slightly soluble in ethanol, and insoluble in diethyl ether or chloroform. The analysis was in agreement with the proposed formula: the chloride content was determined by titrimetric analysis with silver nitrate in acidic medium; the copper content was determined either by atomic absorption spectrophotometry or by iodometric analysis and the organic ligand by UV spectrophotometry ($\lambda = 293$ nm in 1 M $\mathrm{HClO_4}$ aqueous solution). The potentiometric titration of its aqueous solution confirmed the presence of only one mole of acid hydrogen per mole of complex, and the calculated dissociation constant agreed with that reported by Liu [2].

Dihydrogen bis-(pyridine-2-aldoxime)-copper(II) chloride

$$([\mathrm{Cu}(\mathrm{C_6H_5N_2O})_2\mathrm{H_2}]\mathrm{Cl_2} = [\mathrm{Cu(PAO)_2H_2}]\mathrm{Cl_2})$$

was prepared by the slow addition of anhydrous cupric chloride (0.025 mol to a solution of pyridine-2-aldoxime (0.01 mol in about 100 ml chloroform). The mixture was allowed to stand, with stirring, for one hour at least. The pale-green complex was filtered off, washed several times with chloroform and dried in vacuo over silica gel for about 48 h. The analysis, performed as described above, was in agreement with the proposed formula; in this case the potentiometric titration of the aqueous solution of the complex showed the presence of two moles of acid hydrogen per mole of complex, and the calculated successive dissociation constants proved the *cis* configuration of the complex.

Bis-(pyridine-2-aldoxime)-copper(II)

($[Cu(C_6H_5N_2O)_2] = [Cu(PAO)_2]$)

was prepared by dissolving about 2 g of the monohydrogen complex in water, adding sodium hydroxide aqueous solution up to pH *ca.* 9, and extracting several times with chloroform. The organic solvent was evaporated off and the very dark-green residue was washed with ether and dried in vacuo over silica gel for about 48 h. The analysis, performed as described above, was in agreement with the proposed formula; chloride and acid hydrogen were absent.

## Results and discussion

### *Thermogravimetry*

Thermogravimetry in vacuo (Fig. 1) shows that $[Cu(PAO)_2H]Cl$ is stable up to about 160° and then decomposes through three separate steps at least. The first inflection in the TG curve occurs at 53% mass loss, corresponding to 1.5 molecules of ligand; analysis of the evolved gas provides no evidence of chlorine of chloride ion. The intermediate is thermally stable up to about 230°, and could be obtained by interruption of the heating of the sample at 200°. The analysis gave the following results: C 22.7%, H 1.9%, N 8.7% (by elemental analysis), Cu 39.7% (by atomic absorption spectrophotometry), Cl 22.0% (by titration with silver nitrate) and O 5.0%

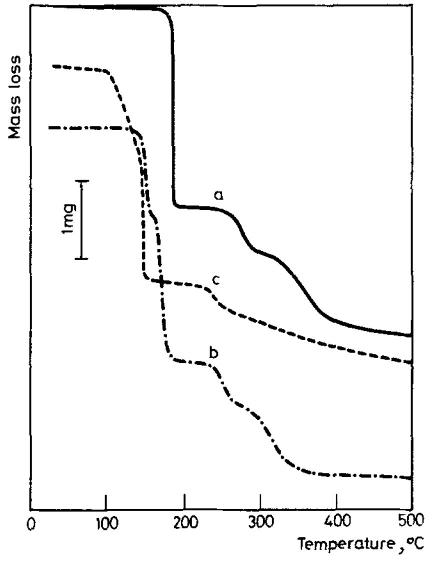

**Fig. 1** Thermogravimetric curves in vacuo for: (a) $[Cu(PAO)_2H]Cl$, (b) $[Cu(PAO)_2H_2]Cl_2$, (c) $[Cu(PAO)_2]$

(by difference), corresponding to the simplest formula $C_6H_6N_2OCu_2Cl_2$ (calcd.: C 22.51%, H 1.89%, N 8.75%, O 5.00%, Cu 39.70% and Cl 22.15%). The spectroscopic characteristics of the intermediate show that the first step of decomposition of the complex occurs with a rearrangement of the ligand. The absorption bands at *ca.* 1720 $cm^{-1}$ in the IR spectrum (KBr disk) and at 265 nm in the UV spectrum (1 *M* $HClO_4$ aqueous solution) allow the hypothesis of the conversion of pyridine-2-aldoxime into acid amide (Beckmann rearrangement). This hypothesis is confirmed by the picolinic acid obtained on hydrolysis of the intermediate in acid medium [12–13]. This thermal decomposition reaction occurs through the copper(II) to copper(I) reduction, as proved by the iodometric analysis of the metal ion. The second inflection in the TG curve occurs between 13% and 17% mass loss, corresponding to amide decomposition; in fact, the UV spectrum of the residue at 325° reveals the loss of aromatic bands. The last decomposition process leads to a residue of metallic copper; the difference between the calculated (18.57%) and found (11–13%) weights is due to the sublimation of copper chloride.

In a dynamic nitrogen atmosphere the initial decomposition temperature is delayed (175°) as in oxygen (Fig. 2); the first inflection occurs between 33% and 40% mass loss. Analysis of the intermediate at 200° (probably a mixture of two compounds) demonstrates that the decomposition reaction again occurs through the copper(II) to copper(I) reduction and the conversion of pyridine-2-aldoxime into acid amide. A clear difference occurs in the last decomposition step, for in oxygen the residue reaches a constant weight at about 470° (calcd. for CuO 23.21%, found 21–23%), while in nitrogen atmosphere the residue continues to lose mass at a slow rate until about 700–800°.

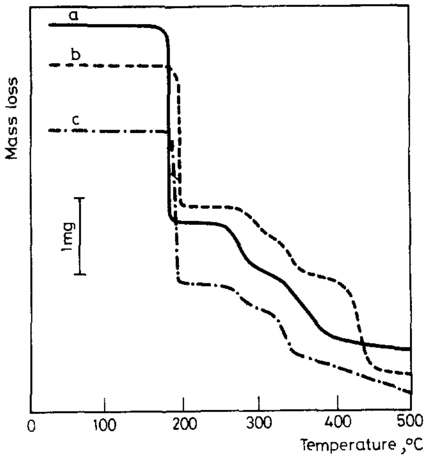

**Fig. 2** Thermogravimetric curves for $[Cu(PAO)_2H]Cl$: (a) in vacuo, (b) in an oxygen atmosphere, (c) in a nitrogen atmosphere

The complex $[Cu(PAO)_2H_2]Cl_2$ begins to decompose at about 130° in vacuo (Fig. 1). On the first step, corresponding to a loss of one mole of chloride per mole of complex, a second process is superimposed, corresponding to partial organic ligand decomposition (*ca.* 58% mass loss). Chemical and spectroscopic analysis of the intermediate at 200° show the formation of a compound very like that found at the same temperature for the "monohydrogen" complex. In this case too the decomposition proceeds through the copper(II) to copper(I) reduction and pyridine-2-aldoxime rearrangement into the acid amide. The decomposition of the intermediate continues between 230° and 500° (two steps) giving a residue of metallic copper (calcd. 16.78%, found 9–10%). TG in dynamic nitrogen and oxygen atmosphere shows the same initial decomposition temperature (*ca.* 130°), but the mass loss at 200° is about 48% and 40%, respectively. Analysis of the intermediate proves the copper(II) reduction and the ligand rearrangement. The successive thermal decomposition process involves two unresolved steps, between about 240–350° and 350° in nitrogen, and 240°–375° and 375°–460° in oxygen.

The complex $[Cu(PAO)_2]$ exhibits the lowest thermal stability; in fact, it begins to decompose at about 100° in vacuo (Fig. 1) and through unresolved steps the complex sustains a mass loss of about 58%, corresponding to 1.5 molecules of ligand. The intermediate, which shows the same chemical (copper(I)) and spectroscopic characteristics (UV and IR spectra) as the previously described intermediates, is stable between 150° and 220°, and then slowly decomposes, leading to a residue of metallic copper (calcd. 20.78%, found 21.5%). In dynamic nitrogen and oxygen atmospheres the initial decomposition temperature is delayed (about 125°), but the stable intermediate is formed at about 150–160° and begins to decompose through unresolved steps at about 230°.

## *DTA studies*

The DTA curves are presented in Fig. 3. The DTA curves for $[Cu(PAO)_2H]Cl$ and $[Cu(PAO)_2]$ are almost identical. In dynamic oxygen atmosphere the first decomposi-

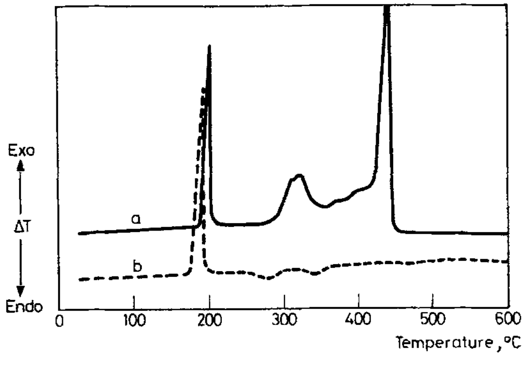

Fig. 3 Differential thermal analysis curves for $[Cu(PAO)_2H]Cl$: (a) in an oxygen atmosphere, (b) in a nitrogen atmosphere

tion process gives one large exothermic peak, while the intermediates decompose to the accompaniment of unresolved large exothermic peaks. The decomposition of $[Cu(PAO)_2H_2]Cl_2$ begins with the absorption of thermal energy, as shown by the initial small endothermic peak in the DTA curve, but the reaction quickly becomes self-sustaining through a large exothermic reaction, as the complex decomposes with the formation of the stable intermediate; this intermediate then decomposes, giving unresolved exothermic peaks. In dynamic nitrogen atmosphere the first decomposition processes of the complexes are not modified; however in this case, the oxidative decomposition of the intermediates produces some small endothermic peaks.

### *Mass spectroscopy*

The gas evolution detection curves for the thermal decomposition of the complexes in vacuo as determined by mass spectroscopy, are almost identical; they show two distinct steps below 300°, with a broad region of gas evolution at higher temperatures (Fig. 4). The mass spectra of the gases evolved at about 170° and 260° (Fig. 5) for $[Cu(PAO)_2H]Cl$ are almost identical to the spectra obtained from pyridine-2-aldoxime [14, 15] and picolinamide [16], respectively, and this confimrs the hypothesis of the proposed decomposition mechanism. There are some small differences in peak groups, due to the thermal fragmentation of the picolinamide bonded to the metal ion. The spectra also verify that no chlorine or chloride products are evolved in these steps. In contrast, the mass spectrum of the gases evolved at about 170° for $[Cu(PAO)_2H_2]Cl_2$ points to the evolution of HCl.

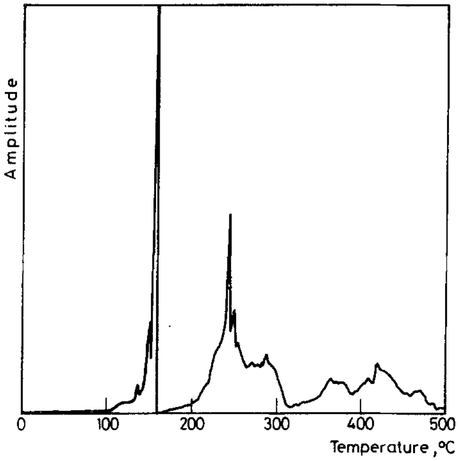

**Fig. 4** Mass spectrometric data of gas evolution resulting from the thermal decomposition of $[Cu(PAO)_2H]Cl$ in vacuo

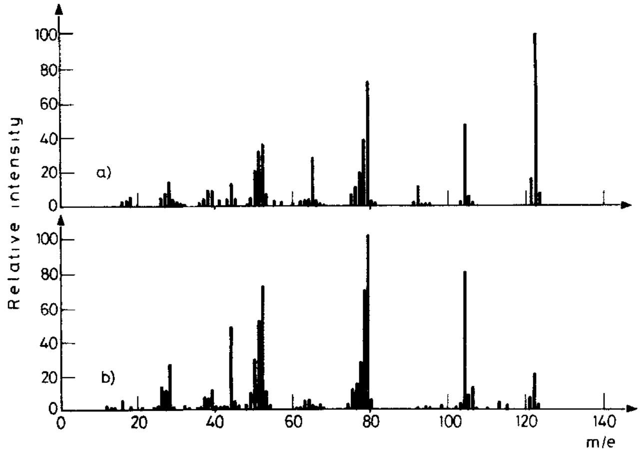

Fig. 5 Mass spectrum of gases evolved from $[Cu(PAO)_2H]Cl$ in vacuo: (a) at 170 °C, (b) at 260 °C

## Conclusion

Pyridine-2-aldoxime can act as a chelating agent, forming a very stable five-membered ring with copper(II) ions. The chemical and potentiometric analyses indicate the general formula $[Cu(PAO)_2H_n]Cl_n$ (where $n = 0$, 1 or 2) and prove the *cis* configuration of the complexes. The spectroscopic data [6] show that the copper ion is in either an essentially square planar environment, or an octahedral environment with a very large tetragonal distortion; the chloride ions are weakly coordinated.

The initial decomposition temperature is influenced by the number of acid hydrogens in the complex; the thermal stability sequence in vacuo is

$$[Cu(PAO)_2H]Cl > [Cu(PAO)_2H_2]Cl_2 > [Cu(PAO)_2]$$

The thermal decomposition reactions of these complexes occur through several separate steps, the first of which involves partial ligand decomposition, the reduction of copper(II) to copper(I), and the conversion of the residual pyridine-2-aldoxime into acid amide. These reactions occur in vacuo, in nitrogen and in oxygen dynamic atmospheres. The hypothesis of this decomposition mechanism is confirmed by the chemical analysis, UV-visible and IR spectroscopic data and mass spectra of the stable intermediates obtained by interrupting the heating of the samples at the appropriate temperatures.

The successive steps correspond to the oxidative decomposition of the intermediates, producing exothermic or endothermic peaks in oxygen or in nitrogen atmospheres.

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**Zusammenfassung** — Die thermischen Eigenschaften einiger Komplexe von Kupfer(II) mit Pyridin-2-aldoxim (HPAO), in denen der Ligand entweder als Ion ($PAO^-$) oder als neutrales Molekül vorliegt, wurden im Vakuum und in dynamischer $N_2$- und $O_2$-Atmosphäre ermittelt. Zur Untersuchung wurden thermoanalytische (TG, DTG, DTA) und spektrometrische (UV-sichtbar, IR, diffuse Reflektionsspektrophotometrie, Massenspektrometrie) Techniken herangezogen. Die Temperatur, bei der die Zersetzung beginnt, wird durch die Zahl der sauren Wasserstoffatome im Komplex beeinflußt; für die thermische Stabilität im Vakuum gilt die Reihenfolge

$$[Cu(PAO)_2H]Cl > [Cu(PAO)_2H_2]Cl_2 > [Cu(PAO)_2].$$

Die thermischen Zersetzungsreaktionen verlaufen in mehreren diskreten Schritten, wobei der erste von diesen eine partielle Zersetzung des Liganden, die Reduktion von Kupfer(II) zu Kupfer(I) und die Konversion des verbleibenden Pyridin-2-aldoxims in das Säureamid in sich einschließt.

**Резюме** — В вакууме и динамической атмосфере кислорода исследованы термические свойства некоторых комплексов двухвалентных меди и пиридин-2-альдоксима (HPAO), в которых лиганд находится как в ионной форме ($PAO^-$), так и в виде нейтральной молекулы. Исследование было проведено термоаналитическими (ТГ, ДТГ, ДТА) методами, электронными спектрами поглощения в УФ- и видимой области, ИК спектроскопией, масс-спектроскопией и спектроскопией диффузного отражения. Начальная температура разложения зависит от числа кислотных водородов в комплексе, а термоустойчивость их в вакууме может быть расположена в ряд

$$[Cu(PAO)_2H]Cl > [Cu(PAO)_2H_2]Cl_2 > [Cu(PAO)_2]$$

Реакции термического разложения протекают в несколько стадий, первая из которых вызывает частичное разложение лиганда, восстановление двухвалентной меди до одновалентной и превращение оставшегося пиридин-2-альдоксима до амида кислоты.